On the Viscosity and Molecular Dimensions of Gaseous Cyanogen.

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The molecule of cyanogen is of particular interest in the theory of molecular structure put forward by Lewis* and Langmuir.† Each cyanogen radicle (CN) is supposed to be practically identical in the arrangement of its outer electrons with the molecule of nitrogen (N_2), except that it lacks one electron. The junction of two CN radicles, to form C_2N_2, is conceived to be brought about by the sharing of one pair of outer electrons, so that the shape of the molecule may be regarded as nearly identical with that of two nitrogen molecules, with their centres at a certain distance apart, at present unknown. A test of the validity of this view is possible on the basis of the theory recently suggested by the author,‡ with reference to the collisions between non-spherical gaseous molecules, provided that the molecular dimensions of N_2 and C_2N_2 deduced from viscosity measurements are known. Reliable values for nitrogen are already available, but not for cyanogen. The viscosity measurements recorded in this paper supply this deficiency.

Experimental Determinations.

The cyanogen was prepared by heating well dried cyanide of mercury in an evacuated hard glass tube, the gas, as it was formed, being pumped off and collected over mercury. A volume of about 50 c.c. at atmospheric pressure was thus prepared, and further purification consisted of fractionating it at the temperature of $-80°$ C. At this temperature cyanogen is solid, but it has an appreciable vapour pressure, so that, by pumping off the vapour and rejecting the early portions, possible impurities such as air and carbon dioxide were removed. The middle part of the fractionation—about 20 c.c.—was preserved over mercury for the viscosity measurements.

The method used for determining the viscosity has already been described in detail.§ Actually, the same apparatus was used as in the author's measurements of the viscosities of the rare inert gases. Only a small quantity of gas was required—about 6 c.c. at atmospheric pressure. The necessary observations are of a very simple character, consisting merely in comparing the times of descent of a mercury pellet between two marks in a vertical tube, when the apparatus is filled with different gases or with the same gas at different temperatures. For further details, the paper just referred to may be consulted. The experiments undertaken were (1) the determination of the ratio of the viscosities of cyanogen and air at atmospheric temperature; and (2) the comparison of the viscosities of cyanogen at steam temperature and at atmospheric temperature. From these results, the absolute data for air being accurately known, those for cyanogen can be deduced. Observations were therefore taken with the apparatus filled at atmospheric pressure alternately with air and cyanogen, both being dried with phosphorus pentoxide just previously to introduction. Each time of transpiration here recorded is the mean of a considerable number—at least ten—consistent amongst themselves to within 1 per cent., and this mean is considered to be reliable to 0·1 or 0·2 per cent. The mercury pellet was about 4 cm. long, and the same one was used throughout.

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* G. N. Lewis, 'Journ. Amer. Chem. Soc.,' vol. 38, p. 762.

† I. Langmuir, 'Journ. Amer. Chem. Soc.,' vol. 41, p. 868.

‡ A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 98, p. 360.

§ A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 84, p. 181.

Temperature 15° C.

Times of transpiration in seconds.		
Cyanogen.	Air.	Ratio, cyanogen/air.
82·95	150·9	0·5497

This ratio of the times of transpiration is somewhat higher than the ratio of the viscosities, on account of the different amounts of slipping of the two gases over the walls of the capillary tube. The mode of applying this correction is indicated in my previous paper (*loc. cit.*), and need not be repeated here. The result obtained is

$$\text{At } 15^\circ \text{ C.}, \frac{\eta_{\text{Cy}}}{\eta_{\text{air}}} = 0{\cdot}548,$$

where η represents viscosity. At this temperature the viscosity of air is $1{\cdot}799 \times 10^{-4}$ C.G.S. units, so that

$$\eta_{\text{Cy}} = 0{\cdot}986 \times 10^{-4} \text{ C.G.S. units at } 15^\circ \text{ C.}$$

The times of transpiration for cyanogen at atmospheric and steam temperatures were as follows:

Cyanogen.

Times of transpiration in seconds.		Ratio, t_{100}/t_{15}.
15° C.	100° C.	
82·95	106·1	1·279

This ratio is approximately equal to the ratio of the viscosities at the two temperatures, but there are various small corrections necessary, including one for the expansion of the apparatus. These have been allowed for by making measurements of the time ratio for air over the same temperature interval, and comparing it with the correct viscosity ratio. Thus the time ratio for air was found to be 1·217. The true viscosity ratio is 1·220 for this temperature interval, so that the total correction is a positive one of 3 parts in 1200. Hence, for cyanogen

$$\frac{\eta_{100}}{\eta_{15}} = 1{\cdot}282,$$

which gives for the absolute value

$$\eta_{\mathrm{Cy}} = 1{\cdot}264 \times 10^{-4} \text{ C.G.S. units at } 100^\circ \text{ C.}$$

If we assume that Sutherland's law holds for the variation of viscosity with temperature, the values of Sutherland's constant (C) and the viscosity at 0° C. (η_0) can be calculated from the above data. The results thus obtained are

$$C = 280,$$

and

$$\eta_0 = 0{\cdot}935 \times 10^{-4} \text{ C.G.S.}$$

The viscosity of cyanogen at 0° C. has been estimated previously from Graham's transpiration experiments in 1846.* The value given is $0{\cdot}95 \times 10^{-4}$ C.G.S. That now obtained is probably more reliable and correct to about 0·2 per cent. The same degree of accuracy cannot be claimed for the figure given for Sutherland's constant, owing to the comparatively small temperature interval to which the measurements were necessarily limited. In this case the probable error is of the order of ten units, or between 3 and 4 per cent.

Calculation of Molecular Dimensions.

A knowledge of both η_0 and C enables us to calculate by means of Chapman's† formula, modified somewhat in its interpretation according to recent suggestions of the author,‡ the mean area presented in collisions by a molecule of cyanogen in the gaseous state. This area proves to be

$$\bar{A} = 1{\cdot}31 \times 10^{-15} \text{ cm.}^2$$

and is probably accurate to about 2 per cent. It is improbable that the cyanogen molecule can be regarded as spherical, and the precise significance of $\bar{A}$ is not apparent unless some definite shape is assigned to the molecule. As mentioned earlier, there are reasons for supposing that C_2N_2 is nearly identical in shape with two linked nitrogen molecules. According to the views of both Lewis and Langmuir, the nitrogen molecule has a very compact arrangement of its outer electrons. Lewis supposes them to be arranged in close pairs at the five corners of two tetrahedrons with a common face; Langmuir assigns a special arrangement with eight outer electrons at the corners of a cube, as in neon and argon, and attributes the inertness of the nitrogen molecule to this disposition. Both these views, and particularly Langmuir's, make the nitrogen molecule comparable with the atoms of the inert monatomic gases. Accordingly, there would appear to be the same justification for regarding N_2 as behaving in collision like a hard elastic sphere as Chapman has shown to be the case for argon, kryptom, and xenon. The diameter of this sphere, obtained from viscosity measurements, is known, and is given by

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* Kaye and Laby's Tables.

† S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279.

‡ A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 98, p. 181.

$$2\sigma = 3{\cdot}15 \times 10^{-8} \text{ cm.,}^*$$

whence

$$\pi\sigma^2 = 0{\cdot}78 \times 10^{-15} \text{ cm.,}$$

$\pi\sigma^2$ being the collision area for the nitrogen molecule, treated as spherical.

It will be seen that the mean collision area of the cyanogen molecule is greater than that of the nitrogen molecule in the proportion

$$\frac{\bar{A}}{\pi\sigma^2} = 1{\cdot}31/0{\cdot}78 = 1{\cdot}68.$$

Let us suppose, with Lewis and Langmuir, that a cyanogen molecule has the size and shape of two nitrogen molecules with their centres at a certain distance apart, and that it behaves in collision like a hard body formed by two overlapping hard spheres each of which has the kinetic properties of a nitrogen molecule. This body will present in collision a target of variable area, the mean value of which is determined by the magnitudes of the constituent spheres and their distance apart. The estimation of this mean area is precisely the same problem as that dealt with by the author in a former paper (*loc. cit.*) in which it was shown that the mean area in question ($\bar{A}$) is given in complete elliptic integrals by

$$\frac{\bar{A}}{\pi\sigma^2} = 1 + \frac{4}{3\pi}\left\{\left(\frac{1}{k}+k\right)E\left(k, \frac{\pi}{2}\right) - \left(\frac{1}{k}-k\right)F\left(k, \frac{\pi}{2}\right)\right\},$$

where σ is the radius of each of the constituent spheres, and k is the ratio d/σ, $2d$ being the distance apart of the centres of the spheres.

If we now identity $\bar{A}$ with the actual mean collision area found experimentally for the cyanogen molecule, and $\pi\sigma^2$ with that of the nitrogen molecule, we can calculate the distance apart of the centres, obtaining thus

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* The value given by Chapman for 2σ is $3{\cdot}10 \times 10^{-8}$ cm. This has been corrected by adopting Millikan's latest value for the number of molecules per cubic centimetre, and by taking into account Kia Lok Yen's recent accurate re-determination of the viscosity of nitrogen ('Phil. Mag.,' vol. 38, p. 582).

$$2d = 2{\cdot}30 \times 10^{-8} \text{ cm.}$$

That is to say, from this point of view, we expect the two cyanogen radicles, each behaving as a nitrogen molecule as regards size and shape, to have their centres at this distance apart, when combined to form C_2N_2. Or, we may say that the diameter of the outer electron shell of the cyanogen radicle is $2{\cdot}30 \times 10^{-8}$ cm.

It is not yet possible to appeal to X-ray crystal measurements for confirmation of this estimate, for cyanide crystals have not hitherto been so examined. Such results will no doubt be obtainable by the same methods as W. L. Bragg* has used so successfully for measuring the dimensions of elementary atoms. It is, however, significant that the crystals of potassium cyanide and those of the potassium halides are usually stated to be isomorphous, and that, in addition, we find that KBr and KCN have nearly identical molecular volumes† —43·1 and 42·8 respectively. Thus if CN replaces Br there is no appreciable change of volume, and we may conclude, tentatively, that the cyanogen radicle and the bromine atom have the same size. Now Bragg's estimate of the diameter of the domain occupied in crystal structure by a bromine atom is $2{\cdot}38 \times 10^{-8}$ cm., and he assigns the value $2{\cdot}35 \times 10^{-8}$ cm. to the diameter of the outer electron shell of this atom. This is remarkably close to the above value $2{\cdot}30 \times 10^{-8}$ cm., which has been deduced for the distance apart of the centres of the two CN radicles in C_2N_2, *i.e.*, in circumstances which involve the sharing of a pair of outer electrons. Should X-ray examination of potassium cyanide prove it to be strictly isomorphous with potassium bromide, therefore, there will be good grounds for regarding the cyanogen radicle and the nitrogen molecule as bearing the relation to one another assumed in the Lewis-Langmuir theory.

An estimate would thus also be provided for the diameter of the outer electron shell of the nitrogen molecule, it being nearly the same as that of the kryptom atom, for the bromine and krypton atoms have the same size. The kinetic behaviour of the two gases confirms this view, since the diameters of the hard spheres to which the nitrogen molecule and the krypton atom are equivalent are $3{\cdot}15 \times 10^{-8}$ cm. and $3{\cdot}19 \times 10^{-8}$ cm., respectively. This is somewhat remarkable, when we consider how different is the number of electrons in the two cases. The nitrogen molecule has only 14, while the krypton atom has 36. It follows that the packing of the electrons must be much closer in the krypton atom than in the nitrogen molecule. A similar statement holds for the bromine and cyanogen molecules, in which the numbers of electrons are 70 and 26 respectively, yet the collision areas are nearly identical,—1·28 as compared with 1·31.

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* W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169.

† Molecular volume here signifies the ratio of molecular weight to crystal density, or the volume per gramme-molecule.

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The Properties and Molecular Structure of Thin Films of Palmitic Acid on Water. Part I.

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The experiments to be described in this paper have been undertaken in order to obtain confirmation of the very interesting views put forward by Langmuir (1) upon the arrangement of the molecules of various substances spread upon the surface of water. The study of these films has been carried on by a number of workers for many years, some of the principal publications being those of Miss Pockels (2), Rayleigh (3, 4), Hardy (5), Devaux (6), and recently Labrouste (7): but in most of these papers the authors do not enter into much detail regarding the molecular structure of the films.

So much information is now available however as to the dimensions of molecules and the forces about them, much of it being of an accurate quantitative nature, derived from structural organic chemistry, from the study of crystals, the kinetic theory of gases and the deviations from the simple gas laws, etc., that an attempt to deduce the arrangement of the constituent molecules from the properties of the films has become something more than a speculation and may be made with some certainty and definiteness.

And conversely, since the films of fatty acids and the other substances investigated appear to be only one molecule in thickness and to have all the molecules arranged in similar orientation—often simply perpendicular to the surface—measurement of the mechanical properties of films consisting of a known number of molecules of a pure substance, affords unusually direct information concerning the force fields round individual molecules. An